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**THE TROPOSPHERIC LIFETIMES OF HALOCARBONS AND THEIR
REACTIONS WITH OH RADICALS:
AN ASSESSMENT BASED ON THE CONCENTRATION OF ^{14}CO**

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EXECUTIVE SUMMARY

Chemical reaction with hydroxyl radicals formed in the troposphere from ozone photolysis in the presence of methane, carbon monoxide and nitrogen oxides provides an important removal mechanism for halocarbons containing C-H and C = C double bonds. The isotopic distribution in atmospheric carbon monoxide has been used to quantify the tropospheric hydroxyl radical distribution. This review reevaluates this methodology in the light of recent chemical kinetic data evaluations and new understanding gained in the life cycles of methane and carbon monoxide. None of these changes has forced a significant revision of the ^{14}CO approach. However, it is now somewhat more clearly apparent how important basic chemical kinetic data are to the accurate establishment of the tropospheric hydroxyl radical distribution.

The two-dimensional (altitude-latitude) time-dependent (seasonal) hydroxyl radical distribution obtained by the ^{14}CO approach has then been used in the Harwell model to estimate halocarbon lifetimes together with their confidence limits. A simple graphical procedure suffices to relate halocarbon lifetime to the pre-exponential factors and activation energy parameters which describe the temperature dependent $\text{OH} + \text{halocarbon}$ rate coefficients. Lifetimes and their 1-sigma confidence limits are calculated using the Harwell two-dimensional model for a range of alternative fluorocarbons.

1. INTRODUCTION

The role of homogeneous gas phase reaction in the lower atmosphere was first investigated in the 1950's, in attempts to understand the phenomenon of photochemical smog and the chemistry involved in its formation (Leighton, 1961). It was Levy (1971) who first suggested that free-radical chemistry, driven by photochemical dissociation of ozone and nitrogen oxides, might be important in the background troposphere. He proposed that relatively high concentrations of the reactive hydroxyl radicals could be maintained in steady state in the background sunlit troposphere and that this steady state could provide an efficient scavenging mechanism for both natural and man-made trace constituents on a global scale.

Since then attempts have been made to unravel the free-radical chemistry of the troposphere and to quantify its role in the trace gas cycles. The reactions of the hydroxyl radical in the troposphere have been linked to a growing list of trace gases including ozone and NO (Levy 1971; Crutzen 1974), carbon monoxide (Weinstock and Niki 1972), methane (Ehhalt 1974), hydrogen (Seiler and Schmidt 1974) followed somewhat later by the sulphur compounds (Crutzen 1976) and halocarbons (Cox et al 1976). This review concerns the distributions of tropospheric hydroxyl radicals and their role in determining the lifetimes of halocarbons. Figure 1 shows some of the species and some of the atmospheric chemical reactions of importance in the global troposphere.

Interest in tropospheric chemistry has been stimulated by the problem of depletion of stratospheric ozone by chlorofluoromethanes and other chlorine-containing species (HMSO 1976; NAS 1977). The extent to which chlorine compounds injected at the earth's surface reach the stratosphere depends on the efficiency with which they are scavenged in the troposphere. Quantitative determination of the sink strength is required to assess the impact of various chlorine-containing species, both natural and man-made, on stratospheric ozone.

The scavenging processes acting in the troposphere may be divided into physical removal processes, in which species are absorbed irreversibly at the earth's surface or in precipitation elements (cloud and rain droplets, aerosols) and chemical removal processes which involve reactions in the atmosphere. Physical removal is often referred to as wet and dry deposition and may be highly efficient for some trace constituents such as ozone, sulphur dioxide and nitric acid. However for halocarbons it is not generally a particularly efficient process and it may be neglected for most species.

Chemical removal of halocarbons by destruction with tropospheric hydroxyl radicals has been shown to be an important sink for those halocarbons which contain H atoms and C=C double bonds, (Cox et al 1976). This sink process may be represented simply by the equation (1), below:



where k is some temperature dependent OH rate coefficient and OH is some form of globally averaged concentration of hydroxyl radicals.

Early two-dimensional model studies (Derwent and Eggleton 1978) have shown that because of the covariance of the temperature dependent value of k , the hydroxyl radical concentration [OH] and the halocar-

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bon concentration itself $[\text{Hal}]$, the lifetime due to OH reaction, τ , cannot be adequately represented by the simple box model equation (2), below:

$$\text{lifetime due to OH reaction} = \frac{\overline{[\text{Hal}]}}{\overline{k [\text{OH}]} [\text{Hal}]} = \frac{1}{\overline{k [\text{OH}]}} \quad (2)$$

The more reactive halocarbons are not distributed uniformly throughout the troposphere and the sink strength reflects only the OH distribution close to the source, normally close to the surface in midlatitudes of the northern hemisphere. The more reactive the halocarbon, the larger the discrepancy between the “true” average OH concentration and that derived from the box model approach. The less reactive halocarbons often exhibit a more marked temperature dependence in their rate coefficients for OH radical attack. This concentrates oxidation close to the surface and makes chemical removal in the middle and upper troposphere relatively unimportant. The less reactive the halocarbon therefore the lower the tropospheric mean temperature required to calculate the mean reaction rate coefficient in equation (2).

For halocarbons of low reactivity with respect to hydroxyl radicals, mean lifetimes may extend to several years. Under these conditions, inter-hemispheric exchange will give a much more uniform distribution between the two hemispheres. As the halocarbon lifetime increases, then fraction of the surface injection which can reach the stratosphere will also increase. For a halocarbon with a lifetime of 10 years, up to 20% of the surface injection could be transported into the stratosphere. On this basis, methyl chloride and methyl chloroform have been identified as significant chlorine carriers to the stratosphere from natural and man made sources, respectively.

An accurate, quantitative assessment of the impact of a given halocarbon on stratospheric ozone, therefore requires a thorough understanding of tropospheric OH destruction. Such an understanding requires information on the following aspects:

- the reaction rate coefficient of the halocarbon with OH radicals, and its variations throughout the troposphere driven by temperature and pressure,
- the tropospheric distribution of OH radicals,
- the transport mechanisms of halocarbons within the troposphere,
- the halocarbon source strength and its spatial distribution,
- the nature and behaviour of any longer-lived degradation products,
- the transport mechanisms of halocarbons to the stratosphere.

Since the 1970s understanding of many of the above areas has grown tremendously as a result of the many field and laboratory investigations which have been carried out, carefully interpreted with theoretical modelling studies. Instrumental techniques and computational models are both areas which have seen impressive and powerful gains in performance which have had repercussions on our understanding on

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atmospheric composition and the influence of man's activities. It is now clearly understood that man has had and continues to have a significant influence on the global concentrations of many trace constituents. The number of species whose tropospheric concentrations have a significant upwards trend is being continually revised. In addition to carbon dioxide, now must be added the chlorofluoromethanes (CCl_3F , CCl_2F_2), carbon tetrachloride, methyl chloroform, methane and ozone, itself. Man's activities will most certainly have had an additional influence of the tropospheric distribution of hydroxyl radicals, however, it is not yet possible to quantify what this influence has been.

The tropospheric distribution of the hydroxyl radical has yet to be unambiguously defined. Despite the pioneering investigations of the KFA Julich group using long path ultraviolet absorption spectroscopy, a reliable climatology of hydroxyl concentrations with adequate three-dimensional and temporal resolution is unlikely to be available in the near future. To advance the assessment process for halocarbons in the absence of an observed tropospheric hydroxyl distribution, recourse has been made to derived or inferred distributions from the following principal sources:

- chemical modelling studies, (Crutzen and Fishman 1977),
- studies of halocarbon behaviour, particularly methyl chloroform, (Singh 1977; Neely and Plonka 1978),
- studies of the isotopic distribution in atmospheric carbon monoxide, (Volz, Ehhalt and Derwent 1981).

The results from all three methods agree relatively well with each other and with the available observations from the KFA Julich group, within their respective estimated confidence limits. It is, however, important to review these different methods and to form a judgement as to whether current understanding is adequate for assessment purposes.

This review addresses the isotopic distribution in atmospheric carbon monoxide with a view to quantifying the tropospheric hydroxyl distribution. The aim is to examine its potential role in removing from the atmospheric circulation, the proposed alternative aerosol propellants, foam blowing agents, solvents and refrigerants which are currently under consideration as replacements for those halocarbons containing chlorine which may reach the stratosphere. This review has been commissioned within the framework of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS).

2. THE ISOTOPIC DISTRIBUTION IN ATMOSPHERIC CARBON MONOXIDE

The first attempts to calculate the global mean tropospheric hydroxyl concentration from isotopic distribution in atmospheric carbon monoxide were made by Weinstock 1969 and by Weinstock and Niki (1972). They used the three available ^{14}CO measurements by McKay et al (1963), an estimate of the global source strength for ^{14}CO from the well-known cosmic ray bombardment of atmospheric nitrogen molecules, the $\text{OH} + \text{CO}$ rate coefficient and derived an estimate for the atmospheric turnover time for ^{12}CO of the order of 1 month. Furthermore, they suggested that OH radicals were responsible for the CO removal and obtained an estimate of their global mean abundance. Seiler (1974) argued that these early measurements of ^{14}CO might be too low and thus have given rise to too short a lifetime and too high a mean tropospheric hydroxyl radical concentration.

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Volz, Ehhalt and Derwent (1981) repeated the methodology and obtained a mean tropospheric hydroxyl radical concentration of $(6.5^{+3}_{-2}) \times 10^5$ molecule cm^{-3} based on four refinements, viz:

- additional measurements of ^{14}CO in the lower troposphere,
- evaluated chemical kinetic data for the $\text{OH} + \text{CO}$ reaction,
- improved life cycle data for ^{14}C and ^{12}C in the troposphere,
- a global two-dimensional time-dependent model to investigate the coupled $\text{CH}_4\text{-H}_2\text{-CO-NO}_x\text{-O}_3$ life cycles, replacing the box model approach.

In the intervening years since the publication of these early studies (Weinstock and Niki 1972; Volz, Ehhalt and Derwent 1981), understanding of the oxidizing capacity of the troposphere has developed significantly. The paragraphs which follow have therefore been devoted to a reevaluation of some of the measurements, data and assumptions which were essential in the Volz, Ehhalt and Derwent (1981) study. The general impression gained from this reevaluation is that subsequent research does appear to have neither undermined nor found the ^{14}CO method seriously flawed. It therefore remains a viable method for determining the tropospheric hydroxyl distribution. Nevertheless, some of the input assumptions could now be questioned in detail and these areas are highlighted and their impact on the determination of the tropospheric hydroxyl distribution assessed.

The Methodology Used

The methodology adopted by Volz, Ehhalt and Derwent (1981) was to take a precalculated two-dimensional (altitude, latitude), time-dependent (monthly) field of tropospheric hydroxyl radicals and linearly scale it until it generated surface ^{14}CO and ^{12}CO concentrations which balanced observations. At the point of balance, the methodology simultaneously determined the tropospheric hydroxyl distribution and the biogenic source strength of ^{12}CO , both of which are coupled unknowns.

The estimated tropospheric hydroxyl distribution contains uncertainties which derive directly from the uncertain ^{14}CO measurements, the uncertainties in the ^{14}CO and ^{12}CO life cycles, the uncertainties in the parameters used in the two-dimensional model and the uncertainties inherent all the assumptions made in the model formulation itself. The uncertainty analysis treatment in Volz, Ehhalt and Derwent (1981) considered the contributions from the likely errors in:

- the ^{14}CO production from cosmic rays, (Lingenfelter 1963),
- the ^{12}CO emission from fossil fuel burning, (Seiler 1974; Logan et al 1981),
- the ^{14}CO measurements, (McKay et al 1963; Volz, Ehhalt and Derwent 1981),
- the ^{12}CO latitudinal distribution, (Seiler and Schmidt 1974),
- the transport and chemistry schemes employed in the two-dimensional model, (Derwent and Curtis 1977).

Experimental Techniques

The measurement of the concentration of ^{14}CO is essential to the ^{14}CO approach. The early measurements of McKay et al 1963 relied on the isotopic ratio viz. $^{14}\text{CO}/^{12}\text{CO}$ in air samples obtained from an air liquefaction plant. McKay et al however failed to determine simultaneously the ^{12}CO concentration and this led to the introduction of uncertainties in using the ^{14}CO approach. A major challenge in the study by Volz, Ehhalt, Derwent and Khedim (1979) was therefore the measurement of the ^{14}CO concentration.

Volz, Ehhalt, Derwent and Khedim (1979) have described their experimental procedures in some detail and only a brief outline is given in the paragraphs below. The procedure consists of two steps,

- the quantitative separation and the collection of the CO from ambient air,
- the determination of its isotopic ratios, $R_{\infty} = [^{14}\text{CO}]/[^{12}\text{CO}]$.

The ^{14}CO concentration is then given by:

$$[^{14}\text{CO}] = R_{\infty} \cdot [^{12}\text{CO}]$$

The separation of the CO from ambient air was achieved by quantitative oxidation to CO_2 on a hot platinum catalyst, followed by absorption in CO_2 -free aqueous NaOH. Prior to this the atmospheric CO_2 was removed from the air sample by absorption in NaOH. Interferences from any remaining CO_2 were determined by gas chromatography and were found to be less than 5%. The CO concentration in the air was measured by gas chromatography and, in addition, calculated from the amount of CO collected and the volume of air sampled, (100-200 m^3).

The isotopic ratio of the sampled CO was measured in a low-level counting system, similar to those used for ^{14}C dating, with an accuracy of $\pm 3\text{-}5\%$. The counting system was calibrated against the ^{14}CO standard of the Institut für Umweltphysik, Universität Heidelberg. The overall accuracy in the determination of the ^{14}CO concentration was largely determined by uncertainties associated with the sampling procedure as discussed by Volz, Ehhalt, Derwent and Khedim (1979), and was generally on the order of $\pm 10\%$ (1σ), including any possible systematic bias.

Measured ^{14}CO Concentrations

So far measurements of the ^{14}CO concentration have been reported only for the northern hemisphere, (Volz, Ehhalt and Derwent 1981). Most of the samples were collected during 1977 and 1978 at a remote, rural site in the Eifel mountains ($51^\circ\text{N } 2^\circ\text{W}$) in the Federal Republic of Germany. In addition, three samples were collected during a cruise of the RV Knorr over the Mediterranean Sea and the Atlantic (36° to 46°N) in April 1976 and two samples at Miami, Florida (27°N) in September 1977, (Volz, Ehhalt, Derwent and Khedim 1979).

The ^{14}CO concentration data exhibit a well-defined seasonal cycle with a winter maximum of about 20 molecule cm^{-3} and a summer minimum of 10 molecule cm^{-3} . The annual cycle in ^{14}CO reflects the influence of the chemical sink due to destruction by tropospheric OH radicals.

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The ^{14}CO concentration data also show evidence of a latitudinal gradient increasing from the equator to the North Pole. The concentrations at Miami (27°N) in September 1972, 4.2 ± 0.7 molecule cm^{-3} are almost a factor of three smaller than those found at 51°N for the same time of year. Similarly, the concentrations measured over the Atlantic Ocean show an increase from 15 molecule cm^{-3} at 36°N to 19 molecule cm^{-3} at 43°N. This latitudinal distribution in ^{14}CO reflects the influence of the tropospheric OH distribution increasing from the North Pole towards the equator.

Evaluated Rate Coefficient Data

An important aspect of the two-dimensional model used to calculate the tropospheric distribution of hydroxyl radicals, is the chemical kinetic input data adopted. Figure 1 illustrates the main free radical reactions which are believed to be occurring in the sunlit free troposphere. To a degree, the OH distribution estimated by Volz, Ehhalt and Derwent (1981) is sensitive to all the chemical kinetic assumptions. However, some of the chemical kinetic input parameters exert a more significant influence on the OH concentrations than others and it is upon these that we have concentrated upon in the paragraphs below. The Volz, Ehhalt and Derwent (1981) paper drew much of its chemical kinetic input data from the 1979 CODATA review (Baulch et al 1980). This can be directly compared with the 1988 IUPAC evaluation (Atkinson et al 1989).

OH to HO_2 interconversion reactions

The conversion of hydroxyl to hydroperoxyl radicals is driven largely by the reaction of OH radicals with carbon monoxide, methane and hydrogen. There has been an important revision in the $\text{OH} + \text{CO}$ rate coefficient over the intervening years from $1.4 \times 10^{-13} (1 + p_{\text{atm}}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $1.5 \times 10^{-13} (1 + 0.6 p_{\text{atm}}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This reevaluation reduces the rate coefficient by 14% at 1 atmosphere pressure and increases it by about 3% under the conditions in the upper troposphere. There have been revisions to the $\text{OH} + \text{CH}_4$ and $\text{OH} + \text{H}_2$ rate coefficients. Under the conditions appropriate to the lower troposphere, the $\text{OH} + \text{CH}_4$ rate coefficient has been increased by about 6%, whereas the $\text{OH} + \text{H}_2$ rate coefficient has decreased by about 4%. Overall, these latter reevaluations are not likely to be significant compared with that of the $\text{OH} + \text{CO}$ reaction.

In the two-dimensional model study, the concentration fields of CO, CH_4 and H_2 were taken from the available measurements and sufficient CO, CH_4 and H_2 were injected into the model at every time step to balance removal by all processes in the surface layer including the reaction with hydroxyl radicals. If a lower $\text{OH} + \text{CO}$ rate coefficient had been employed then, to maintain the same $\text{OH} \rightarrow \text{HO}_2$ flux, a 10-15% higher OH concentration would be required.

HO_2 to OH interconversion reactions

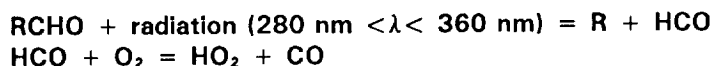
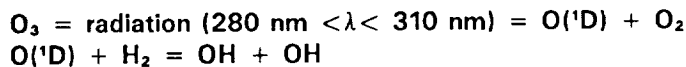
The conversion of HO_2 radicals to OH radicals is largely driven by the reactions of HO_2 radicals with ozone and nitric oxide. The rate coefficients of these two reactions under conditions appropriate to lower troposphere have not changed by more than 1-7%. These reevaluations are of negligible importance.

HO_2 recombination to form hydrogen peroxide

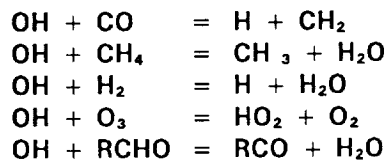
The recombination of HO_2 radicals to form hydrogen peroxide dominates free radical termination in the free troposphere at all heights and latitudes where NO_x levels are low. The reaction has generally

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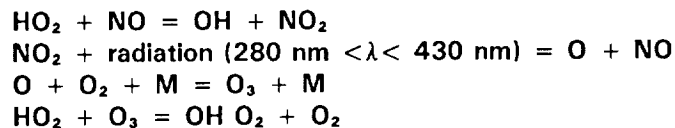
Free Radical Production



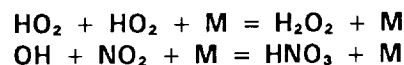
HO to HO₂ Interconversion



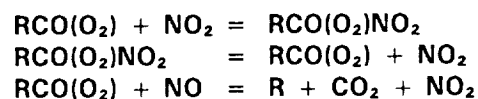
HO₂ to OH Interconversion



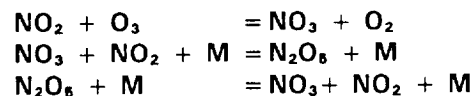
Free Radical Loss Processes



Temporary Reservoir Formation



Nighttime Chemistry



Heterogeneous Processes

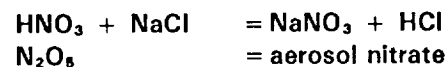


Figure 1. The main species and atmospheric chemical reactions of importance in the global troposphere.

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not been intensively investigated in laboratory chemistry studies and evaluations have had only a few studies to draw upon. It is not surprising to find that this reaction has undergone a dramatic reevaluation between the 1979 CODATA (Baulch et al 1980) and 1988 IUPAC (Atkinson et al 1989) studies. The unusually large negative activation energy reported previously has been replaced by a significantly smaller but nevertheless still negative value. The effect of the reevaluations is to produce a $\text{HO}_2 + \text{HO}_2$ rate coefficient which is about a factor of 1.7 lower in the lower troposphere and a factor of 4 lower in the upper troposphere.

Because of the square dependence of the free radical destruction rate on the HO_2 radical concentration, the reevaluation of the $\text{HO}_2 + \text{HO}_2$ rate data should lead to OH and HO_2 radical concentrations about a factor of two higher in the upper troposphere and about thirty percent higher in the lower troposphere.

The reevaluations in the chemical kinetic data indeed strengthen the results of Volz, Ehhalt and Derwent, 1981: at the time of their evaluation, the OH concentrations required to balance the budgets of both ^{12}CO and ^{14}CO were a factor of 1.7 greater than those derived from photochemical models. It appears now that inadequacies in the chemical kinetic data, most important the rate coefficients for the OH +

Table 1. The budget for atmospheric carbon monoxide (^{12}CO) as estimated by Volz, Ehhalt and Derwent (1981) and compared with a more recent assessment (Seiler and Conrad 1987)

Source Strength, g yr^{-1}	^{14}CO Methodology	Present View
Terpenes and isoprene	$1150 \times 10^{12}\text{a}$	1000×10^{12}
Ocean ^b	100×10^{12}	100×10^{12}
Methane oxidation	$880 \times 10^{12}\text{c}$	600×10^{12}
Man made sources ^c	640×10^{12}	640×10^{12}
Biomass burning	-	1000×10^{12}
Sink Strength, g yr^{-1}		
OH oxidation	$2450 \times 10^{12}\text{d}$	2000×10^{12}
Surface removal	$320 \times 10^{12}\text{e}$	390×10^{12}
Stratospheric removal	-	110×10^{12}
Total Source Strength, g yr^{-1}	2770×10^{12}	3300×10^{12}
Total Atmospheric Mass, g	480×10^{12}	550×10^{12}
Lifetime, yrs	0.17	0.17

Notes:

- a. calculated assuming mass balance.
- b. Seiler (1974). Logan (1981).
- c. Seiler (1974).
- d. from Derwent and Curtis (1977).
- e. Liebl and Seiler (1976).

CO and $\text{HO}_2 + \text{HO}_2$ reactions, indeed resulted in too low OH concentrations in the photochemical models at that time. With the revised rate coefficients, the OH distributions from ^{14}CO and from photochemical models are in much better agreement.

Life Cycle Data

Inherent in the methodology were some basic assumptions concerning the methane, carbon monoxide, hydrogen, nitrogen oxides and ozone life cycles in the two-dimensional model of ^{14}CO and in the two-dimensional model used to estimate the hydroxyl radical concentrations, themselves. At the point where the ^{12}CO and ^{14}CO distributions balanced, the methodology returned the biospheric source strength of ^{12}CO allowing a solution to the ^{12}CO budget.

In Table 1, this budget is examined in some detail and compared with a more recent evaluation by Seiler and Conrad (1987). The overall conclusion is that the broad features of the carbon monoxide budget have remained unchanged. In detail, though, there is a major difference in the significance given to biomass burning. The Volz, Ehhalt and Derwent (1981) study was unable to resolve the difference between biomass burning, on the one hand, and terpene and isoprene oxidation on the other, as both are sources of ^{14}CO and ^{12}CO . Subsequently, field campaigns in the tropical regions of South America have led to a quantification of this source as shown in Table 1.

The inclusion of the biomass burning source would have an impact on the Volz, Ehhalt and Derwent (1981) analysis because of the different latitudinal distributions of the ^{12}CO and ^{14}CO source strengths.

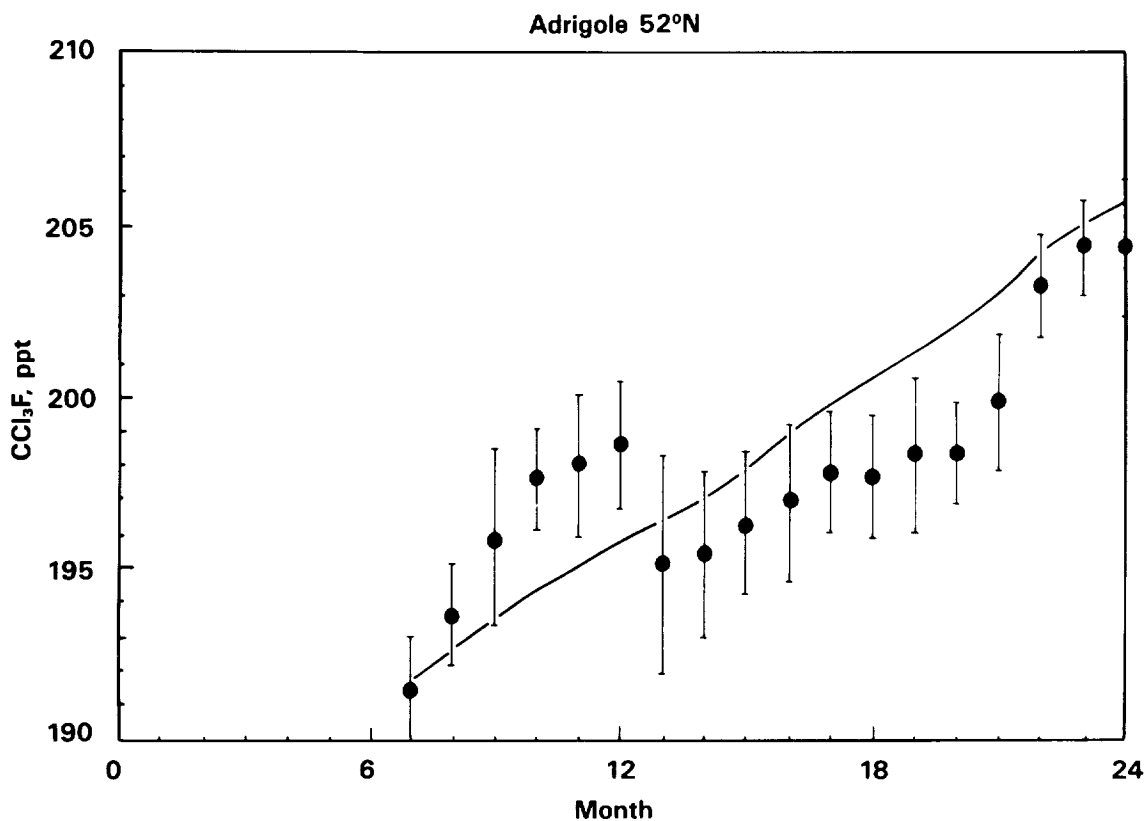


Figure 2. The time series of CCl_3F concentrations at Adrigole 52°N (Cunnold et al. 1986) and the two-dimensional model results.

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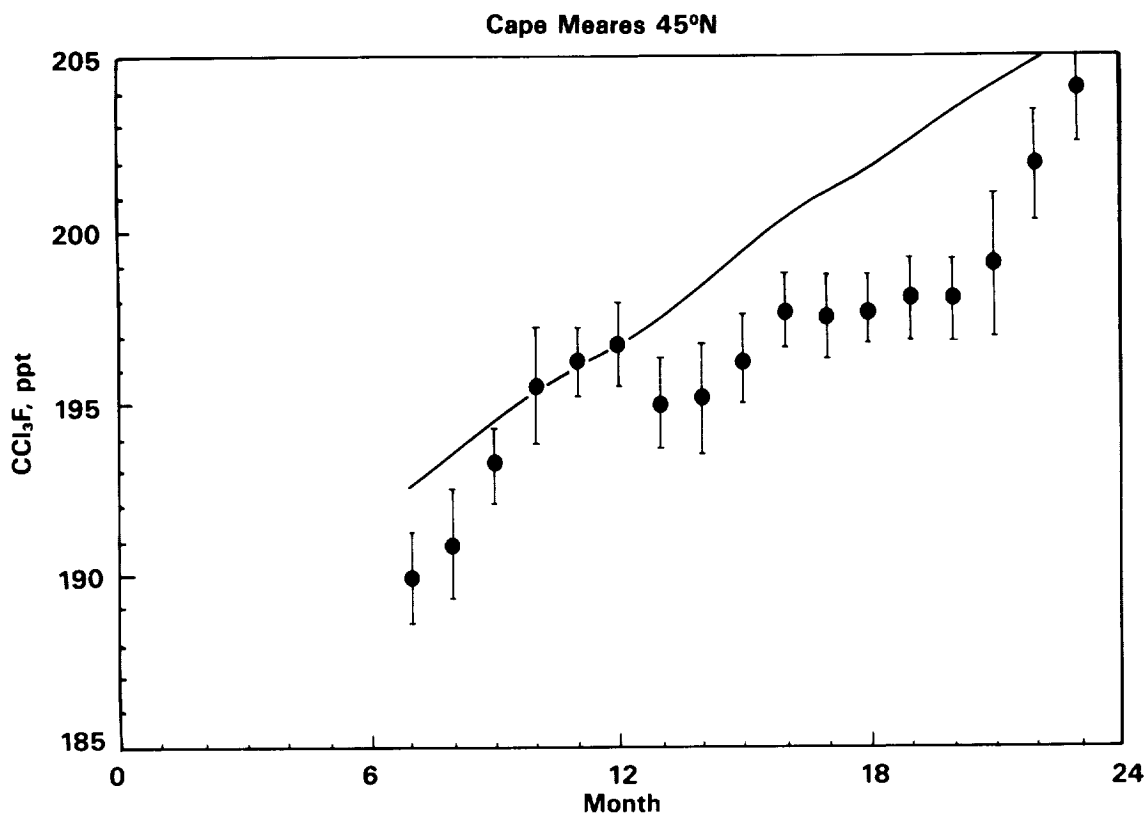


Figure 3. The time series of CCl_3F concentrations at Cape Meares 45°N (Cunnold et al. 1986) and the two-dimensional model results.

The difference is minor because ^{14}CO is rather insensitive to this source and is unlikely to have seriously distorted the 2-D model study.

The revised $\text{OH} + \text{CO}$ rate coefficient has a direct influence on the evaluation of the tropospheric OH distribution through the ^{14}CO life cycle. An important source of ^{14}CO is located in the upper troposphere where the $\text{OH} + \text{CO}$ rate coefficient has been reevaluated. A fixed ^{14}CO injection was assumed so that the increase in $\text{OH} + \text{CO}$ rate coefficient would lead to a decreased ^{14}CO penetration into the free troposphere. The reduced $\text{OH} + \text{CO}$ rate coefficient at the surface would reduce ^{14}CO fluxes there. Overall the $\text{OH} + \text{CO}$ rate coefficient reevaluation would induce small changes in the tropospheric OH distribution of the order of $\pm 7\%$, downwards. The biospheric source strength of ^{12}CO would accordingly require downwards revision to about $1000 \times 10^{12} \text{ g yr}^{-1}$. This latter estimate of the ^{12}CO source strength is identical with the more recent assessment of Seiler and Conrad (1987) quoted in Table 1.

Two-dimensional model transport data

The version of the Harwell two-dimensional model used by Volz, Ehhalt and Derwent (1981) had 7 vertical layers of 2.5 km depth and 18 latitude ranges weighted equally by the sine of latitude. Transfer between the boxes both horizontally and vertically was driven by advection and turbulent mixing. The zonally averaged wind fields were taken from Newell et al (1972) and the eddy diffusion coefficients from Louis (1975).

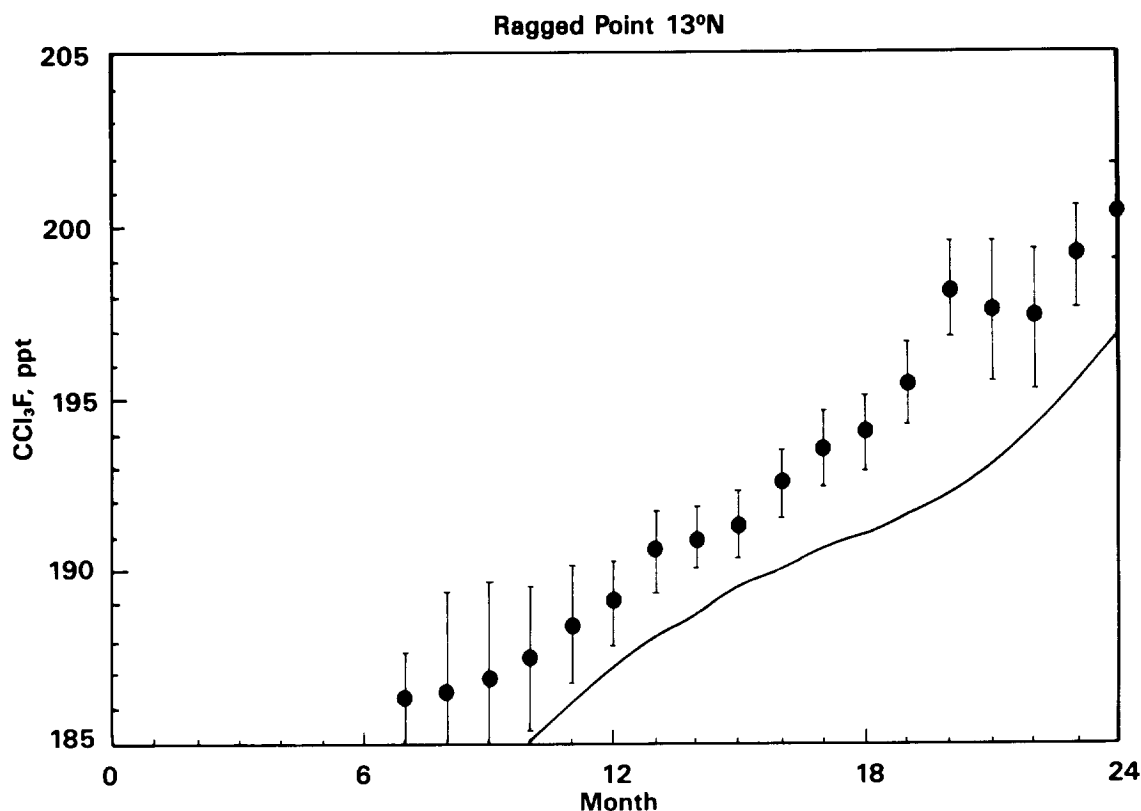


Figure 4. The time series of CCl_3F concentrations at Ragged Point 13°N (Cunnold et al. 1986) and the two-dimensional model results.

The sensitivity of the tropospheric OH distribution derived from the ^{14}CO approach to changes in the transport parameters was investigated by Volz, Ehhalt and Derwent (1981). They concluded that large changes in the transport coefficients of up to a factor of two increase or decrease made little difference to the tropospheric OH distribution required to balance the ^{12}CO and ^{14}CO life cycles. The estimated tropospheric OH distributions changed by less than $\pm 20\%$.

In the intervening years since the first studies with the Harwell two-dimensional model, the ALE experiment has made available high quality halocarbon emissions and time series concentration data for a wide latitude range covering both hemispheres (Cunnold et al 1986). These halocarbon measurements provide an excellent database to validate the transport schemes in two-dimensional models.

The CCl_3F emissions for the period 1931-1982 (Chemical Manufacturers Association 1983, 1988) were used in the Harwell two-dimensional model and an upper boundary condition was applied representing stratospheric photolysis, adjusted to give a CCl_3F lifetime in the range 50-75 years.

Figures 2-6 illustrate the model calculated and measured concentrations of CCl_3F at Adrigole, Republic of Ireland (52°N 10°W) Cape Meares, Oregon (45°N , 124°W), Ragged Point, Barbados (13°N 59°W), Point Matatula, American Samoa (14°S , 171°W) and Cape Grim, Tasmania (41°S , 145°E) for the eight-

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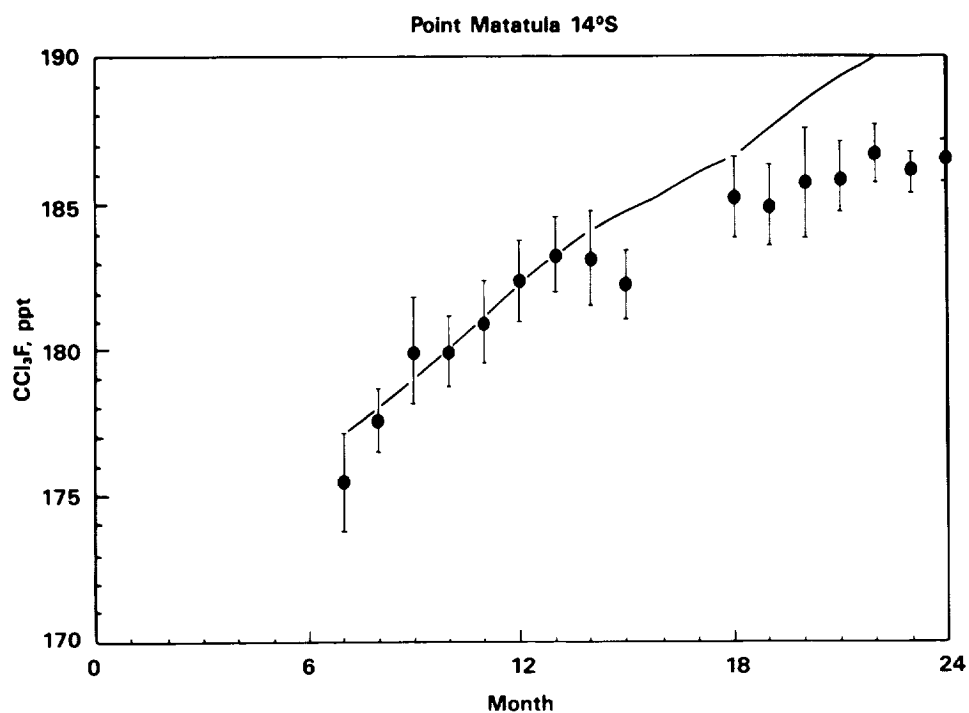


Figure 5. The time series of CCl_3F concentrations at Point Matatula 14°S (Cunnold et al. 1986) and the two-dimensional model results.

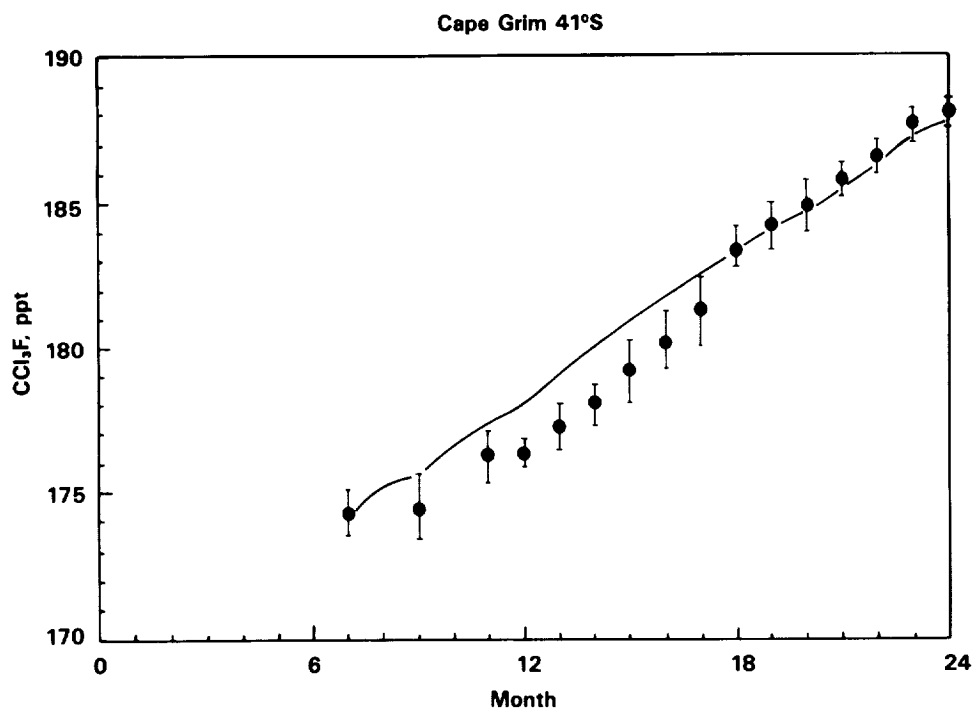


Figure 6. The time series of CCl_3F concentrations at Cape Grim 41°S (Cunnold et al. 1986) and the two-dimensional model results.

een month period from July 1981 to December 1982 (Cunnold et al 1986). Viewed against the ALE measurements, the transport scheme in the Harwell two-dimensional model is clearly performing adequately and without systematic bias.

The conclusion is that the transport scheme adopted in the Volz, Ehhalt and Derwent (1981) study represents adequately the gross features of halocarbon transport and this is an important model validation. Furthermore, the sensitivity of the estimated tropospheric OH distribution to the magnitudes of the transport coefficients is not strong. It is unlikely therefore that inadequacies in present understanding of global transport have seriously influenced the uncertainty in the estimated tropospheric OH distribution using the ^{14}CO method.

3. THE TROPOSPHERIC DISTRIBUTION OF OH RADICALS AND HALOCARBON LIFETIMES

Halocarbon Lifetimes

The behaviour of a halocarbon in a two-dimensional (altitude-latitude) atmosphere injected at the earth's surface, subject to stratospheric destruction and oxidation by hydroxyl radicals can be described by the differential equation:

$$\begin{aligned} \frac{d}{dt} [\text{Hal}] + \text{div} ([\text{Hal}] \cdot \mathbf{U}) - \text{div} (\mathbf{K} \cdot \text{grad} ([\text{Hal}]/N)) \\ = E - k[\text{OH}][\text{Hal}] - \text{SL}[\text{Hal}] \end{aligned} \quad (3)$$

The time behaviour of the halocarbon concentration $[\text{Hal}]$ in molecule cm^{-3} was computed by solving the above continuity equation over a 6×18 mesh point grid extending vertically in 2.5 km steps and in 18 steps latitudinally with equal spacing in $\sin \phi$ where ϕ is the latitude angle. The two-dimensional wind field, \mathbf{U} , and the eddy diffusion tensor, \mathbf{K} , were taken from Newell et al (1972) and Louis (1975), respectively. The detailed procedures used in the finite-differencing scheme have been described elsewhere (Derwent and Curtis 1977). The finite difference form of the above equation was integrated numerically using the Harwell program FACSIMILE (Curtis and Sweetenham 1987). For a 100 year model simulation, 15 minutes computer time were required using an IBM compatible 80386/80387-based microcomputer (Dell System 310).

The terms in the above continuity equation describing the halocarbon behaviour were derived as follows:

- E : a time-independent halocarbon injection was assumed with a spatial distribution which closely followed the population distribution between the hemispheres,
- SL : stratospheric loss coefficient, which was set to give a lifetime due to stratospheric removal, acting on its own, of 50-100 years,
- $[\text{OH}]$: this is the time dependent two-dimensional distribution of tropospheric hydroxyl radicals determined by Volz, Ehhalt and Derwent (1981) and illustrated in figure 7,
- k : this is the temperature dependent rate coefficient for hydroxyl radical attack on the halocarbon of interest.

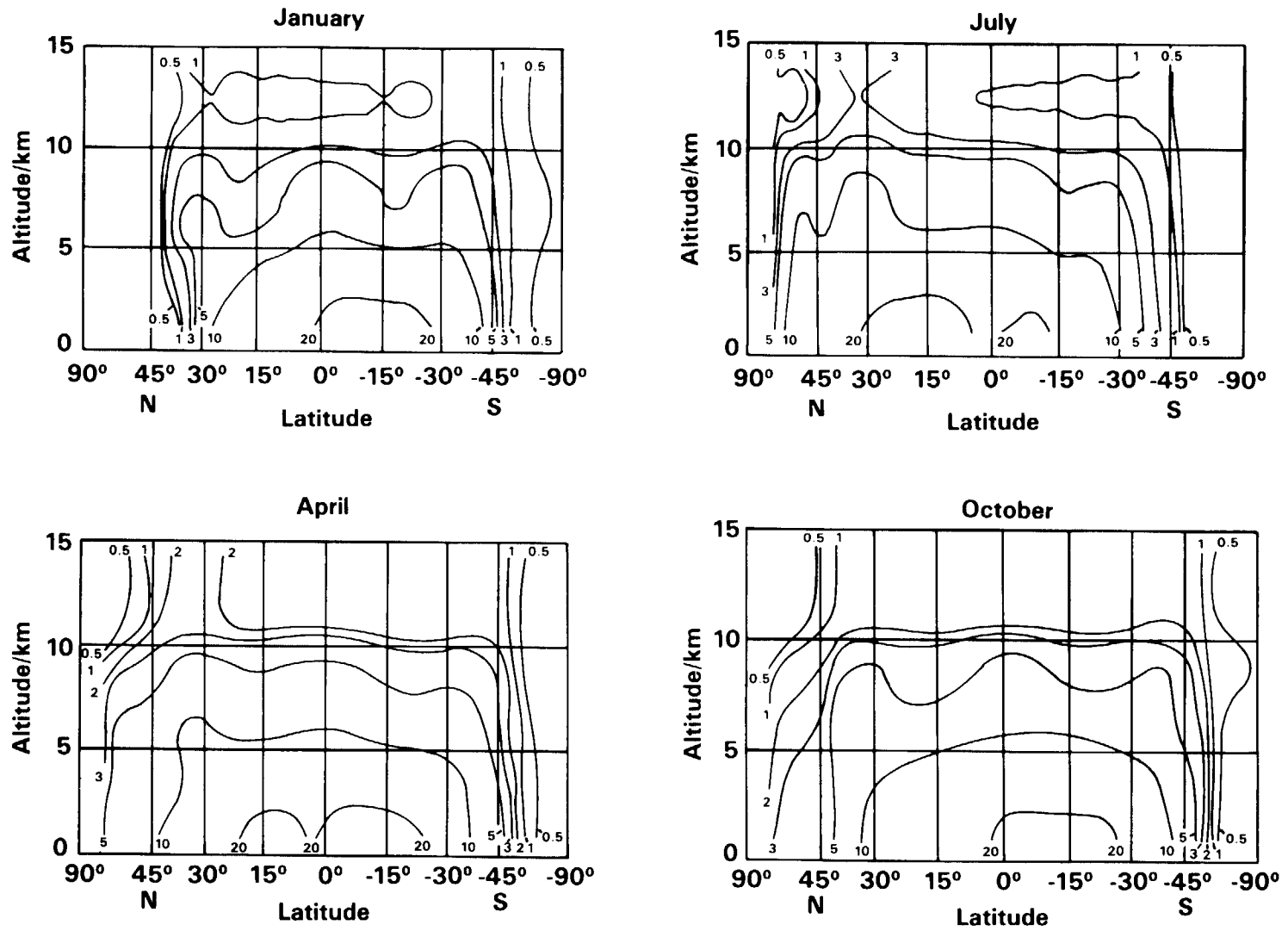


Figure 7. Distribution of hydroxyl radicals ^{14}CO method in $10^5 \text{ molecule cm}^{-3}$

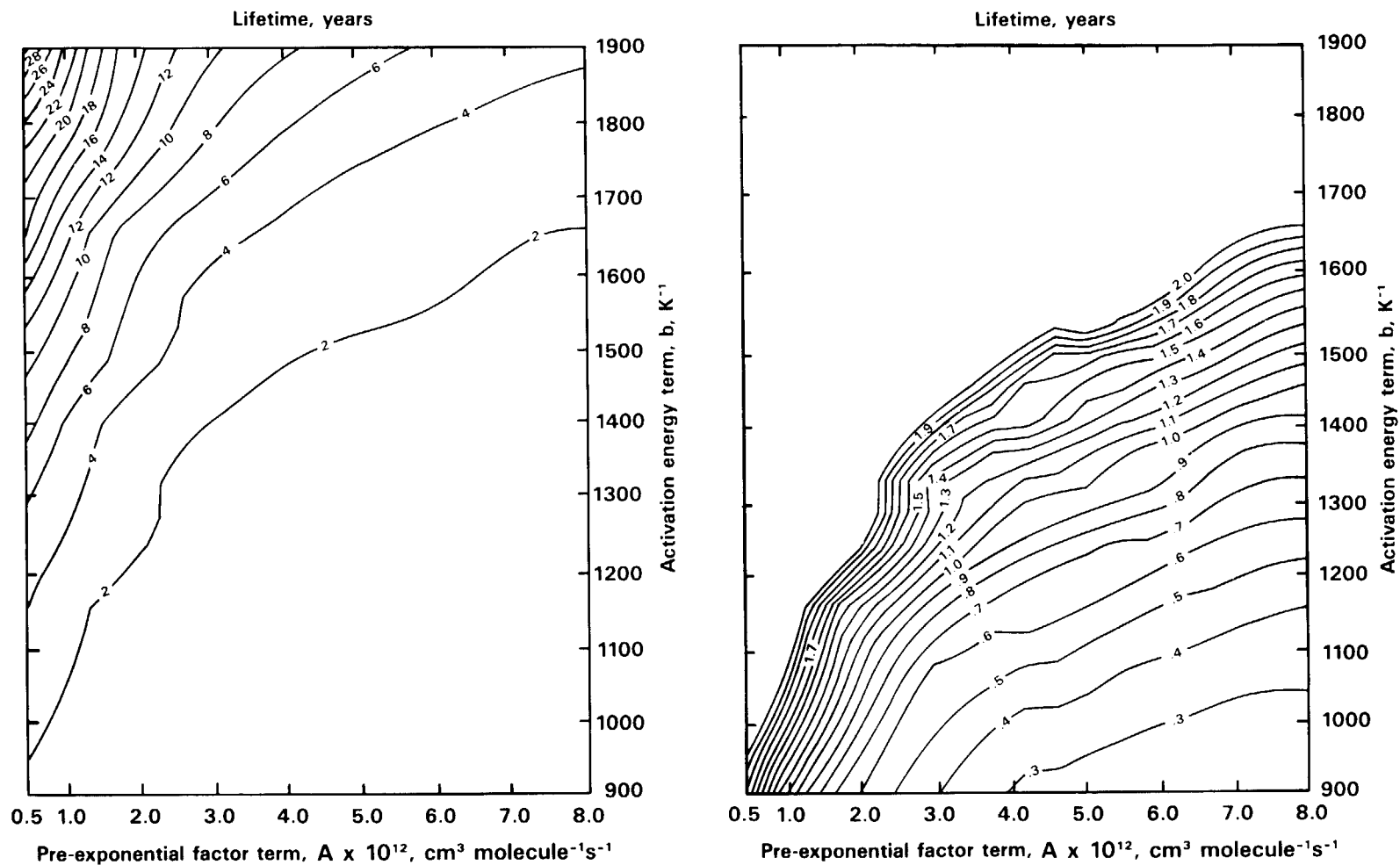


Figure 8. Halocarbon lifetimes in years determined by the ^{14}CO method for halocarbons reacting with OH radicals with a rate coefficient of $A \exp (-b/T)$ where T is the temperature in K.

TROPOSPHERIC LIFETIMES

At the end of the 100 year model experiment, the total model halocarbon inventory was divided by the total halocarbon injection rate to determine the halocarbon lifetime. The assumption of fixed tropospheric hydroxyl radical concentrations implies low tropospheric halocarbon loadings so as not to perturb the tropospheric hydroxyl radical concentrations. For reactive halocarbons, this implies that halocarbon concentrations are not more than 1 ppb at the most.

Figure 8 shows the total lifetimes including both tropospheric OH oxidation and stratospheric removal calculated for various assumptions concerning the form of the temperature dependent OH + halocarbon rate coefficient. Clearly, this temperature dependent parameter exerts a dominant influence on halocarbon lifetime, with lifetimes covering 0.2 - 30 years for reasonable ranges in expected values of preexponential factors and activation energies.

However the ^{14}CO method is not uncertainty-free and its accuracy and precision as a means of determining halocarbon lifetime is dependent on a whole range of experimental, life cycle and modelling assumptions which may be called into question. Volz, Ehhalt and Derwent (1981) gave some thought to uncertainty limits on their tropospheric OH distribution which this reevaluation has not changed. They recommended a mean tropospheric OH concentration of 6.5^{+3}_{-2} molecule cm^{-3} . Assuming that the kinetic parameters defining the OH + halocarbon rate coefficient are described with complete certainty, we can use the 1-sigma confidence limits for the tropospheric OH distribution to determine the confidence limits of the halocarbon lifetime. The Harwell two-dimensional model was therefore rerun with the entire tropospheric OH distribution scaled upwards and downwards to the 1-sigma confidence limits. The resulting upper and lower 1-sigma confidence limits of the halocarbon lifetimes encompassed the range of a factor of two for all the halocarbons examined. Lifetimes were apparently slightly more accurately determined for the longer-lived halocarbons, reflecting the influence of the assumed constant stratospheric removal.

Lifetimes of Alternative Fluorocarbons

For some of the candidate alternative fluorocarbons evaluated chemical kinetic data for the OH + halocarbon degradation reactions are already available, Table 2. The lifetimes of these halocarbons due to stratospheric removal and tropospheric OH radical degradation can therefore be determined using the Harwell two-dimensional model. Table 2 gives the atmospheric lifetimes calculated for a constant injection in mid-latitudes of the northern hemisphere from a 100 year model calculation. The tropospheric OH distribution calculated with the ^{14}CO method gives lifetimes for the alternative fluorocarbons in the range 0.3-635 years. For most of the alternative halocarbons, these lifetimes are considerably shorter than the corresponding lifetimes for the fully halogenated halocarbons.

To complete the environmental acceptability work, modelling studies are required following up the behaviour of any chlorine-containing molecular fragments produced by the halocarbon degradation. The behaviour of the fragments could readily be incorporated into the two-dimensional model to determine the magnitude of any stratospheric fluxes of species such as COCl_2 , COHCl , CF_3COCl , CFCl_2CHO , $\text{CFCl}_2\text{CO}(\text{O}_2)\text{NO}_2$, CF_2ClCHO , $\text{CF}_2\text{ClCO}(\text{O}_2)\text{NO}_2$, COFCl and so on. Competing processes for these chlorine-containing fragments would include tropospheric degradation, dry deposition, photolysis and wet scavenging.

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Table 2. OH + halocarbon rate coefficients and atmospheric lifetimes for a range of alternative fluorocarbons

Formulae	OH + halocarbon rate coefficient, cm ³ molecule ⁻¹ s ⁻¹	Lifetime, ^c yrs Stratospheric loss	None
CH ₃ F	5.4 x 10 ⁻¹² exp(-1700/T)	3.12	3.33
CH ₂ F ₂	2.5 x 10 ⁻¹² exp(-1650/T)	5.40	6.0
CHF ₃	7.4 x 10 ⁻¹³ exp(-2350/T)	46.35	635.0
CH ₂ FCI	3.0 x 10 ⁻¹² exp(-1250/T)	1.23	1.26
CHFCI ₂	1.2 x 10 ⁻¹² exp(-1100/T)	1.74	.80
CHF ₂ CI	1.2 x 10 ⁻¹² exp(-1650/T)	10.35	13.0
CH ₃ CH ₂ F	1.3 x 10 ⁻¹¹ exp(-1200/T)	0.31	0.31
CH ₂ FCH ₂ F	1.7 x 10 ⁻¹¹ exp(-1500/T)	0.59	0.60
CH ₃ CHF ₂	1.5 x 10 ⁻¹² exp(-1100/T)	1.42	1.46
CH ₂ FCHF ₂	2.8 x 10 ⁻¹² exp(-1500/T)	2.98	3.17
CH ₃ CF ₃	2.6 x 10 ⁻¹³ exp(-1500/T)	22.29	40.2
CHF ₂ CHF ₂	8.7 x 10 ⁻¹³ exp(-1500/T)	8.64	10.4
CH ₂ FCF ₃	1.7 x 10 ⁻¹² exp(-1750/T)	10.40	13.1
CHF ₂ CF ₃	3.8 x 10 ⁻¹³ exp(-1500/T)	17.06	25.9
CH ₃ CFCl ₂	2.7 x 10 ⁻¹³ exp(-1050/T)	5.89	6.68
CH ₃ CF ₂ CI	9.6 x 10 ⁻¹³ exp(-1650/T)	12.49	16.6
CH ₂ ClCF ₂ CI	3.6 x 10 ⁻¹² exp(-1600/T)	3.28	3.51
CH ₂ ClCF ₃	5.2 x 10 ⁻¹³ exp(-1100/T)	3.80	4.11
CHCl ₂ CF ₃	6.4 x 10 ⁻¹³ exp(-850/T)	1.36	1.40
CHFCICF ₃	6.6 x 10 ⁻¹³ exp(-1250/T)	4.99	5.54

Notes:

- Chemical kinetic data from Hampson, Kurylo and Sander (1989)
- T is absolute temperature in K
- Lifetimes in steady state have been determined in a two-dimensional model assuming a northern hemispheric and constant injection rate, allowing for either 2% yr stratospheric removal or not
- The 1-sigma confidence limits on the lifetimes encompass a range of a factor of two.

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4. CONCLUSIONS

A review of the ^{14}CO method for determining the tropospheric hydroxyl radical distribution has revealed a number of areas where changes have occurred since the original publication of Volz, Ehhalt and Derwent (1981). None of these changes has however forced a revision of the approach. They have served to complete our understanding of areas which were difficult to understand in the early work. The chemical kinetic data is notable in this regard. It is now much easier to understand why the early hydroxyl radical concentrations may have been under-estimated in the photochemical models as compared to the ^{14}CO evaluation.

For the expected $\text{OH} + \text{halocarbon}$ chemical rate coefficient parameters defined in terms of preexponential factors and activation energies, it is possible to estimate resulting halocarbon lifetimes using a simple graphical procedure. The ^{14}CO approach allows the determination of tropospheric halocarbons lifetimes, halocarbons with reasonable precision, 1-sigma confidence limits spanning about a factor of two.

It is important to remember that $\text{OH} + \text{halocarbon}$ rate coefficients, hydroxyl distributions and halocarbon concentrations exhibit important covariance terms so that halocarbon lifetimes are not well-determined quantities. The lifetimes determined in this review are valid only for halocarbons injected at the northern hemisphere surface over the latitude range of the major continental land masses and population centres.

To illustrate the ^{14}CO method, the graphically determined lifetimes for methane and methyl chloroform are found to be 7^{+3}_{-2} and 5 ± 2 years, respectively, which are in close accord with our two-dimensional model studies (Cox and Derwent 1981; Derwent and Eggleton 1978), and current literature evaluations (Ehhalt 1988; Prinn 1988). The current methyl chloroform lifetime overlaps the ALE/GAGE evaluation, $6.3^{+1.2}_{-0.9}$ years and confirms both estimates since they are completely independent.

Lifetimes of some candidate alternative fluorocarbons have been tabulated in Table 2 based on detailed studies using the Harwell two-dimensional model. These studies should be readily extended to include the subsequent transport and fate of the secondary degradation products liberated by OH attack on the parent halocarbon.

There is mounting evidence that man's activities are inducing changes in the composition of the global atmosphere (Rowland and Isaksen 1988). Some of the trace gases for which global trends are beginning to become characterised play an important role in global tropospheric chemistry, as described in figure 1. In considering the environmental acceptability of alternative fluorocarbons, an attempt should be made to investigate their tropospheric sinks in future scenarios in which the composition of the global troposphere has been grossly perturbed by man's activities. For example, future subsonic aircraft operations may increase local tropospheric OH concentrations (Derwent 1982) and other perturbations can be put forward that would decrease tropospheric OH concentrations. A scenario approach could help to put upper and lower bounds on the lifetimes of alternative fluorocarbons over the next 50 years.

5. ACKNOWLEDGEMENTS

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